

EXTRACTION OF IRON WITH METHYLETHYLKETONE

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16. Abstract The extraction of iron(III) with methylethylketone as solvent from hydrochloric acid solution is described, and the maximum range of acid concentration for quantitative extraction determined. Most of the elements of the third analytical group were investigated for their extractibility with this ketone, and the advantages of this compound are illustrated. Separation of iron from several other elements is possible. The separation from aluminum and manganese is described.			
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1. Introduction

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The extraction of iron(III) from acidic solutions with diethyl ether was recommended for analytical separations as early as 1892 [7]. This method has been tested in detail and is quite often used. But in spite of its frequent application, diethyl ether has various disadvantages in comparison to other solvents for the extraction of iron: The extraction can be done only within a limited acid range; the complete extraction is difficult because of partial photochemical reduction to the non-extractable iron(II); furthermore, the high volatility, flammability, and the peroxide formation of the extractant should be mentioned. In addition, the diethyl ether must be pretreated with hydrochloric acid if it is to be used for extraction of iron(III).

In attempts at improvement, di-isopropyl ether and dichlorodiethyl ether provided advances. Ethers with even greater molecular weights offer no advantage over di-isopropyl ether [1]. The disadvantage of di-isopropyl ether is the high concentration of hydrochloric acid (7.5-8.5 N) which is required for quantitative extraction of iron. Also, the distribution coefficient becomes unfavorable as the iron concentration of the solution decreases. This means that repeated supplemental extraction is necessary, especially if the amounts of iron to be determined are small.

* Numbers in the margin indicate pagination in the original foreign text.

Detailed studies by Specker showed that organic solvents with the groups >C=O or >P=O are especially well suited for the extraction of iron(III) [2, 8]. Ketones have some advantages over diethyl ether: For the same working conditions, the extraction coefficient is higher than with diethyl ether; they form no peroxides; and they are less volatile. The agent in this series which has been studied most is methylisobutylketone (MIBK) [6]. Comparison of the extraction coefficients of diethyl ether (100), diisopropyl ether (1000) and MIBK (5000) shows that MIBK gives the fastest quantitative extraction satisfactorily. The best hydrochloric acid concentration here is about 7 N.

But increase of the extraction coefficient is paralleled by a decrease in the selectivity. The selectivity can be increased, though, by addition of inert solvents [9]. Other ketones have also been studied with respect to their applicability as extraction agents for separation of iron [1].

Glaassen and Bastings attempted to avoid the disadvantages in the extraction with MIBK by using various mixtures of MIBK and amyl acetate as extractants [3].

The present work will describe the extractability of iron(III) with methylethylketone mixed with carbon tetrachloride. This ketone was first applied in 1965 for the selective separation of selenium [5]. We could establish that it offers several advantages in comparison to other solvents. We note first the easy separability of the two phases after the extraction. Also, after shaking, the organic phase appears in the lower / 303 part of the separatory funnel, which is a great advantage in doing the work. No emulsion formation occurred in our studies. The distribution ratio was almost constant over the concentration

range which we studied (3-100 mg iron). No bad effect of high concentrations of nitrate or sulfate on the extraction could be detected. We should also comment on the economy of using this extractant, which has the best price of all the agents under consideration.

2. Experimental Part

Figure 1 shows the behavior of iron(III) with respect to a mixture of methylethylketone-carbon tetrachloride (30:20) as the extracting agent at increasing concentrations of hydrochloric acid, after double extraction.

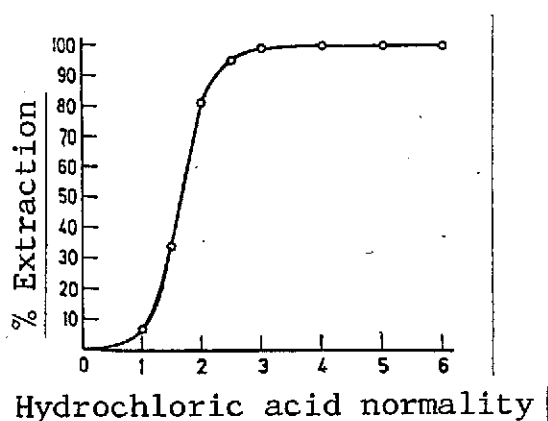


Figure 1. Extraction behavior of iron(III) as a function of the hydrochloric acid concentration. Iron: 26.0 mg.

From the figure, it can be seen that two-fold extraction gives maximum extraction at as low as 3.5 N hydrochloric acid. This can be a particular advantage if there are other elements in the aqueous phase after separation of the iron, and if a low hydrochloric acid concentration is favorable for their determination. The figure also shows that the acid normality in the extraction can vary over a wide range (3.5-6 N).

Table 1

Iron(III) mg	Percent Extraction		
	Hydrochloric Acid Concentration, N		
	4	5	6
3	97	98,1	99,9
5	97	98,5	99,9
7	96,8	98,1	100,3
10	97	98,1	100,0
15	96,9	98,0	99,8
20	97,1	98	100,2
40	97	99	100,2
60	97,2	98,5	99,8
100	97	98	100

Table 1 shows the dependence of the amount of iron extracted on the acid normality after single (!) extraction and a shaking period of 1 minute.

It appears that no dependence of the extraction effect on the amount of iron added could be observed in the concentration range (3-100 mg iron) which we determined.

Procedure

The aqueous iron(III) solution is made 4-6 N in hydrochloric acid in a 50 or 100 ml volumetric flask and filled to the mark. Twenty milliliters of this solution is transferred to a 250 ml separatory funnel. The mixture of 30 ml methylethylketone + 20 ml carbon tetrachloride is added, and the combination is shaken for about 20 seconds. In the meantime it is briefly deaerated once. If the phase separation does not occur quickly

after the shaking, a few drops of carbon tetrachloride are added to the solution, so that the desired effect occurs in a short time without more shaking. After separation of the phases, the organic phase in the lower part of the separatory funnel is drained into a second separatory funnel.

For certainty, the aqueous phase is shaken once more with the ketone-carbon tetrachloride mixture (30:20). The two organic phases are combined, and the iron is re-extracted by shaking twice with 40 ml of water each time. Now the metal can be determined, either with EDTA, by back-titration against thorium nitrate, or with the Reinhardt-Zimmermann method. Both final determinations can be done quickly and reproducibly. If a photometric method is used, however, the small amounts of ketone which are transferred into the aqueous phase must be removed by fuming with sulfuric acid. If a brown color appears, it is removed with a few drops of nitric acid. This method takes longer, but it also gives good values. The ratio of 20 ml aqueous phase to 50 ml organic phase (30 ml methylethyl ketone + 20 ml carbon tetrachloride) proved optimal for the extraction. The distribution coefficient is maximum at this ratio.

Addition of carbon tetrachloride is necessary for two reasons. The ketone is highly soluble in water, and even completely soluble at high concentrations of hydrochloric acid, so that it would not be usable for our purpose. The addition of carbon tetrachloride in the stated proportion suppresses the solubility of the ketone in hydrochloric acid solutions to a minimum. For another reason, the carbon tetrachloride makes the solution denser. This, as mentioned previously, is advantageous in performing the work.

Reagents

Methylethylketone, Merck, highest purity; carbon tetrachloride; hydrochloric acid, highest purity.

3. Separation of Iron from the Elements of Analytical Group III

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Table 2 describes the extractability of the elements of the third analytical group from a 6N hydrochloric acid solution with methylethylketone dissolved in carbon tetrachloride. The amount of metal used per extraction was 50 mg, and the volume of the test solution was 20 ml.

Table 2.

Element	Ti	Al	Cr(III)	U	Mn(II)	
% Extraction	0	0	0	14	0	

Element	Co	Ni	Zn	Th	Ga	In
% Extraction	0,1	0	6,5	0	100	100

Data on the extractability of vanadium could not be produced in an unambiguous manner, because reduction to vanadium(IV) occurred during the shaking process. V(IV) could not be extracted, in any case.

This shows that iron can be separated from titanium, aluminum, chromium, manganese, nickel and thorium without the other elements in the solution appearing in the organic phase. We studied the separations of iron and manganese

Table 3. IRON-MANGANESE SEPARATION FROM 6 N HYDROCHLORIC ACID SOLUTION

Sample	Iron, mg		Manganese, mg	
	Added	Found	Added	Found
1	100,5	100,2	12,8	12,9
2	82,2	82,5	25,5	25,8
3	68,8	68,3	38,3	38,4
4	77,8	77,4	38,3	38,3
5	55,4	55,4	50,8	51,1
6	25,5	25,6	76,3	76,5
7	14,7	14,8	101,6	101,8
8	9,5	9,8	125,5	125,4

Table 4. IRON-ALUMINUM SEPARATION FROM 6 N HYDROCHLORIC ACID SOLUTION

Sample	Iron, mg		Aluminum, mg	
	Added	Found	Added	Found
1	142,6	142,8	12,5	12,5
2	98,7	98,8	25	24,9
3	79,6	79,4	50	49,8
4	79,6	79,6	75	74,9
5	47,5	47,5	75	74,9
6	47,5	47,6	100	100
7	19,0	19,2	150	149,2

(Table 3) and iron and aluminum (Table 4) at varying concentration conditions. The determination of the metals after the extraction was done as follows: Iron, by the Reinhardt-Zimmermann method, or with EDTA by back titration against thorium nitrate; aluminum, complexometrically by back-titration against zinc sulfate with SAS-SN + Erio B as indicator [4]; manganese according to Vollhard-Wolff, EDTA and spectrophotometric.

We also performed a separation with a steel sample from the Federal Institute for Materials Testing (Berlin-Dahlem). Sample composition: Mn, 1.53%; Fe, 68.82%; Cr, 17.56%; Ni, 10.49%; Mo, 0.213%; Nb, 0.74%; Ta, 0.04%; Cu, 0.1%; Co, 0.1%; V, 0.04%. Found: Mn, 1.55%; Fe, 68.5%.

The manganese was determined photometrically in the aqueous phase after separation of the iron. The iron was determined after re-extraction with EDTA by back-titration with thorium nitrate and by the method of Reinhardt-Zimmermann.

The aluminum in the aqueous phase after separation of the iron was determined directly with EDTA in a back-titration procedure with zinc sulfate, using SAS-SN + Erio B as the indicator [4]. Note that an approximately 0.2% aqueous indicator solution was used for the titration. Use of the solid indicator powder proved unsatisfactory because the presence of small amounts of ketone in the aqueous phase reduced the solubility of the dye, so that the color change was not sharp.

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